



Catalytic reactions of bis- π -allylpalladium generated from allyltrifluoroborate

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ABSTRACT

Bis- π -allylpalladium-catalyzed nucleophilic allylations to aldehydes **2** and imines **3** have been achieved by replacing allylstannanes with allyltrifluoroborate. Amphiphilic bisallylation of activated olefins **6** with allyltrifluoroborate and allyl acetate also proceeded smoothly in the presence of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ and tricyclohexylphosphine catalysts.

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Since the discovery of carbon–carbon bond formation in π -allylpalladium complexes¹ with carbon nucleophiles,^{2–4} palladium has become one of the most useful metals in organic synthesis.^{5,6} The π -allylpalladium complexes are key electrophilic intermediates in the Tsuji–Trost allylation reaction and react with various nucleophiles.

In previous studies, we found that bis- π -allylpalladium complexes⁷ react with electrophiles, such as aldehydes⁸ and imines,^{9,10} in a nucleophilic manner (Fig. 1). The presence or absence of ligands controls the reactivity of the bis- π -allylpalladium complexes,¹¹ and they undergo chemoselective allylic addition to aldehydes or imines in the absence of phosphine ligands.¹² Furthermore, bis- π -allylpalladium complexes display amphiphilic reactivity with activated olefins to give the bisallylated products 1,7-octadienes in high yields.¹³ This catalytic amphiphilic bisallyla-

tion can be applied to the synthesis of medium-sized carbocycles.¹⁴ Wallner and Szabó demonstrated the detailed regio- and stereoselectivity of bis- π -allylpalladium complexes by density functional calculations.^{15,16} Recently, Itami and co-workers discovered the regioselective unsymmetrical tetraallylation of C_{60} using the catalytic amphiphilic bis- π -allylpalladium reaction.¹⁷ Not only bis- π -allylpalladium complexes but also pincer-type π -allyl-Pd-Ar complexes display nucleophilic allylation to electrophiles.^{18,19}

In general, in addition to bis- π -allylpalladium formation from the dimerization of butadienes,²⁰ bis- π -allylpalladium complexes utilized for nucleophilic allylation and amphiphilic bisallylation may be generated by the transmetalation of π -allylpalladium complexes with allylstannanes in a catalytic cycle. However, there are disadvantages to the use of organostannanes because of their toxicity as well as their byproducts. We focused on the use of allyltrifluoroborate in catalytic bis- π -allylpalladium reactions. Since the discovery of the Suzuki–Miyaura coupling reaction,²¹ much attention has been paid to organoboranes. The most interesting feature of organoboranes and their byproducts is that they are less toxic compared to other organometallic reagents, in particular, organostannanes. Recently, potassium trifluoroborates, among the other organoboranes, have been utilized widely as equivalents to the corresponding organoboronic acids for Suzuki–Miyaura-type coupling reactions due to their stability, achieved without decreasing their high reactivity.²² Malinakova and co-workers demonstrated palladium-catalyzed bisfunctionalization of allenyl esters for synthesis of unsaturated γ -lactones.²³ Furthermore, Lewis acid²⁴ or palladium-catalyzed²⁵ allylations and the allylation in a biphasic medium ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$)²⁶ of carbonyl compounds have been developed by using allylic boranes and/or borates. In this Letter, we describe an alternative catalytic system of bis- π -allylpalladium complexes generated from allyltrifluoroborate.

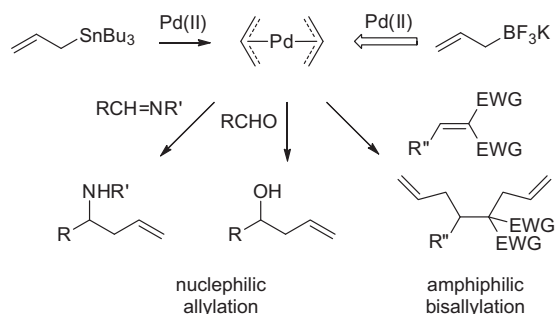


Figure 1. Catalytic reactions of bis- π -allylpalladium.

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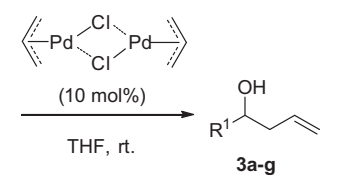
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We first examined the reaction of allyltrifluoroborate **1**²⁷ and benzaldehyde **2a** in the presence of PdCl₂(PPh₃)₂ (10 mol %) in THF at 70 °C. The corresponding homoallyl alcohol **3a** was obtained in 67% yield. Although the use of a palladium(0) catalyst, such as Pd(PPh₃)₄, afforded a lower yield of **3a** (43% yield), the use of π -allylpalladium chloride dimer gave the best result, and the allylation reaction proceeded in 86% yield at room temperature (Table 1, entry 1). Previously, we found that the use of platinum catalysts was more suitable for the nucleophilic allylation of aldehydes with allyltrifluoroborates.^{8,9} We examined this nucleophilic allylation with various aldehydes. As shown in Table 1, 4-bromobenzaldehyde underwent nucleophilic allylation very smoothly to give the corresponding homoallylic alcohol **3b** quantitatively, without giving any allylated product at a bromo-substituted position obtained by the Suzuki–Miyaura-type coupling reaction (entry 2).^{28,29} Not only aromatic aldehydes **2a–c** (entries 1–3) but also aliphatic aldehydes **2d–f** underwent the nucleophilic allylation reaction in the presence of the π -allylpalladium chloride dimer catalyst in THF at room temperature. Cyclohexancarboxaldehyde **2d** gave a lower yield of the homoallylic alcohol **3d** due to the steric hindrance of the cyclohexyl group, while the less hindered *n*-heptanal afforded the corresponding homoallylic alcohol **3d** in 94% yield (entry 4 vs 5). The nucleophilic allylation also proceeded with the conjugated aldehyde **2g** to give **3g** in 65% yield (entry 7).

We then examined the nucleophilic allylation of various imines under palladium(II)-catalyzed conditions. The results are summarized in Table 2. The aromatic imines **4a**, **4b**, and **4c** derived from 4-nitrobenzaldehyde reacted with potassium allyltrifluoroborate **1** to give the corresponding homoallylamines **5a**, **5b**, and **5c**, respectively, in high yields (Table 2, entries 1–3). The aromatic imines **4c** and **4d** derived from benzaldehyde also gave the corresponding homoallylamines **5c** and **5d** in 97% and 66% yields, respectively (entries 4 and 5). The pyridyl moiety substituted on the N-atom of imine **4d** was expected to co-ordinate with the palladium catalyst to accelerate the reaction rate. However, this pyridyl moiety was not effective in this reaction. The reactions of **4f**, derived from 4-tolaldehyde and 4-methoxyaniline, and **4g**, derived from cinnamaldehyde and 4-methoxyaniline, also proceeded smoothly to give the corresponding homoallylamines **5f** and **5g** in 85% and 84% yields, respectively (entries 6 and 7).

The aldehydes and imines underwent the palladium-catalyzed nucleophilic allylation and the corresponding homoallylic alcohols and imines were obtained in good-to-high yields. We investigated the amphiphilic bisallylation of activated olefins **6** in the presence of palladium catalysts. We first examined the optimization of palladium catalysts and ligands for the amphiphilic bisallylation. The

Table 1
Allylation of various aldehydes **2**

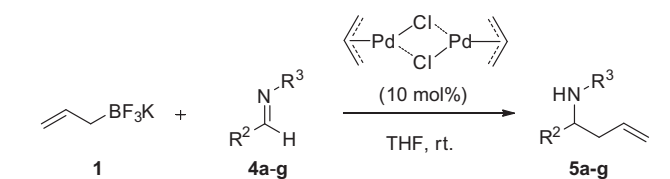


Entry	2	R ¹	Time (h)	Yield ^a (%)
1	2a	Ph	12	86
2 ^b	2b	4-BrC ₆ H ₄	6	>99
3	2c	2-Naphthyl	18	67
4	2d	<i>c</i> -Hexyl	24	53
5	2e	<i>n</i> -Hexyl	24	94
6	2f	PhCH ₂ CH ₂	11	70
7	2g	PhCH=CH	9	65

^a Isolated yield based on aldehyde **2**.

^b The reaction was carried out using PdCl₂(PPh₃)₂ (10 mol %).

Table 2
Allylation of various imines **4**

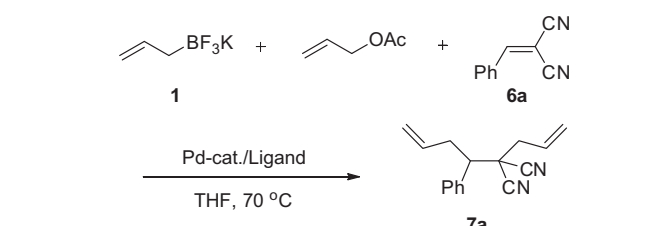


Entry	4	R ²	R ³	Time (h)	Yield ^a (%)
1	4a	4-NO ₂ C ₆ H ₄	Ph	24	93
2	4b	4-NO ₂ C ₆ H ₄	4-CO ₂ MeC ₆ H ₄	7	85
3	4c	4-NO ₂ C ₆ H ₄	4-OMeC ₆ H ₄	7	98
4	4d	Ph	Ph	24	97
5	4e	Ph	2-Py	24	66
6	4f	4-MeC ₆ H ₄	4-OMeC ₆ H ₄	24	85
7	4g	PhCH=CH ₂	4-OMeC ₆ H ₄	24	84

^a Isolated yield based on imine **4**.

results are shown in Table 3. The reaction of phenylidene malononitrile **6a** (1 equiv), allyltrifluoroborate **1** (1.5 equiv), and allyl acetate (1.5 equiv) in THF proceeded in the presence of Pd(PPh₃)₄ (10 mol %) in an Ar atmosphere at 70 °C to give the corresponding bisallylated product **7a** in 71% yield (entry 1). However, the use of allyl chloride, which was considered the most appropriate for the amphiphilic bisallylation with allyltrifluoroborate, was less effective (entry 2). Palladium(II) catalysts, such as Pd(OAc)₂ and PdCl₂(PPh₃)₂, were not effective in this reaction. Therefore, we examined the effect of phosphine ligands on the amphiphilic bisallylation using Pd₂(dba)₃·CHCl₃ (5 mol %). Although tri-*n*-butylphosphine was more effective than triphenylphosphine (entry 1 vs 3), other trialkylphosphines, such as tri-*tert*-butylphosphine and tri-*n*-propylphosphine, afforded low yields of **7a** (entries 4 and 5). The best result was observed in the case of tricyclohexylphosphine, in which **7a** was obtained quantitatively (entry 6). Triphenylphosphite was also a suitable ligand for the reaction (entry 7); however, bidentate phosphines, such as 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)ferrocene (dppf), tripentafluorophenylphosphine, and X-phos³⁰ were not effective in this reaction (entries 8–11).

Table 3
Effect of various ligands on catalytic amphiphilic bisallylation



Entry	Pd-cat. (mol %)/ligand (mol %) ^a	Time (h)	Yield ^b (%)
1	Pd(PPh ₃) ₄ (10)	18	71
2 ^c	Pd(PPh ₃) ₄ (10)	18	38
3	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/P(<i>n</i> -Bu) ₃ (10)	24	85
4	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/P(<i>t</i> -Bu) ₃ (10)	24	42
5	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/P(<i>n</i> -Pr) ₃ (10)	24	30
6	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/PCy ₃ (10)	4	>99
7	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/P(OPh) ₃ (10)	12	80
8	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/dppe (5)	24	38
9	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/dppf (5)	24	3
10	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/P(C ₆ F ₅) ₃ (10)	24	4
11	Pd ₂ (dba) ₃ ·CHCl ₃ (5)/X-Phos (10)	24	30

^a Amount of catalyst and ligand are indicated in the parenthesis.

^b Yield was determined by GC analysis using *n*-dodecane as an internal standard.

^c Allyl chloride was used instead of allyl acetate.

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